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(54) **Process for obtaining polyolefins with broad bimodal or multimodal molecular weight distributions**

Verfahren zur Gewinnung von Polyolefinen mit breiter bimodularer oder multimodaler
Molekulargewichtsverteilung

Procédé d'obtention de polyoléfines possédant de larges distributions de poids moléculaires
bimodales ou multimodales

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COMMUNICATIONS, vol. 14, no. 12, December
1993, pages 765-770, XP000411902**

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Description

[0001] This invention relates to a process for obtaining broad bimodal or multimodal molecular weights.

STATE OF THE ART

[0002] It is known that some metallocenes such as bis(cyclopentadienyl) titanium or dialkyl zirconium in combination with aluminium alkyls as co-catalyst form homogeneous systems which are useful for the polymerisation of ethylene. German patent 2,608,863 describes the system of dialkyl bis(cyclopentadienyl) titanium with trialkyl aluminium.

[0003] The controlled hydrolysis of aluminium alkyls leads to the formation of species which include Al-O bonds called aluminoxanes. Kaminsky et al. (Adv. Organomet. Chem. 18, 99, 1980) have demonstrated that aluminoxanes in combination with chlorinated metallocenes produce very active catalytic systems for the polymerisation of ethylene. The need to reduce or eliminate aluminoxanes, as these are highly flammable, and are used in large proportions in relation to the metal in polymerisation reactions, led to the use of bulky boron compounds which replaced the aluminoxane in stoichiometric molar relationships with respect to the metal of the metallocene, as described in the patents by Turner, EP 277004 and Ewen et al., EP 426637. The metallocenes used in these patents should be dialkyl derivatives, as boron compounds do not have any alkylating capacity. Alkylated metallocenes are highly unstable with water, oxygen and air, with the result that a large proportion of the metallocene present becomes deactivated before polymerisation starts, as it is used up in reacting with the impurities which are present in the medium which have not been eliminated previously. This does not happen when aluminium compounds such as aluminoxane are used, as these act to eliminate impurities from the reaction medium avoiding deactivation of the metallocene.

[0004] The use of metallocenes in combination with aluminium alkyls and aluminoxanes and boron compounds has been described by Razavi et al. in CA 2,027,144 for the polymerisation of syndiotactic polyolefins, with the objective of using small quantities of aluminium compound to remove the impurities and alkylate the metallocene. More recently, Chien et al. (Macromol. Chem. Macromol. Symp., 66, 141-156, 1993) have also used small quantities of aluminium alkyls, generally triethyl aluminium or triisobutyl aluminium, with the same object of removing impurities and alkylating the chlorinated metallocene, finally adding the boron compound as an activator for the reaction. This system makes it possible to use chlorinated metallocenes, which are stable in air, reducing the amount of aluminium compounds in the catalyst system.

[0005] On the other hand these authors comment that the use of these alkyl aluminiums together with these

boron compounds is not obvious, because secondary β -H elimination reactions, or reactions with the boron compound which interfere with the catalytic system, may occur. Many patents have appeared in the last year claiming the use of these mixed co-catalyst systems, e.g. Mitsubishi Petrochemical Co. Ltd. (EP 574258, JP 5295021); Tosoh Corp. (JP 5339316, JP 5310829, JP 5301919, EP 570982, JP 5255423, JP 5239140); Idemitsu Kosan Co. Ltd. (JP 5331219, WO 9324541, JP 5320258-60, JP 5320245-48, JP 5271339, JP 5262823, JP 5262827, JP 5043618); Mitsui Toatsu (JP 5155927, JP 5140221). All these patents claim the use of a smaller quantity of aluminoxane as advantages in the use of mixed co-catalysts, and greater activity and better properties for the polymer, such as e.g. improved processability, high heat resistance, and good transparency.

[0006] In particular, JP 5295021 and JP 5043618 disclose a catalyst comprising a boron compound and an aluminoxane. However, the boron compound used in both cases are different from the boron compounds used in the instant invention. In addition, the boron compounds used in JP 5295021 (trimethylboron and triphenylboron) belong to the category of those compounds which cannot be significantly ionize the metallocene but are usually added to the catalyst as a scavenger or a modifier, i.e., JP 5295021 does not disclose a catalyst system which comprises two compounds which are effective as a cocatalyst in combination with a metallocene.

[0007] The term "bimodal or multimodal molecular weight distribution" means that two or more peaks of different molecular weight can be seen in chromatograms obtained by gel chromatography (GPC), which represent the molecular weight as a function of the relative proportion of polymer having a specific molecular weight.

[0008] Polyolefins which have bimodal or multimodal molecular weight distributions, like polyethylene, can be transformed into articles by extrusion moulding, hot shaping, spin moulding, etc., and in general their most common applications are for tubing, films and articles made by the blowing technique. The advantages over other polyolefins which do not have multimodal molecular weight distributions are easier and faster processing with a reduced energy requirement. In addition to this, bimodal polyolefins show less flow disturbances when molten and are preferred on account of their improved properties such as a better balance between rigidity and resistance to cracking through environmental agents.

[0009] There are in the literature different ways to obtain polymers with broad bimodal or multimodal molecular weight distributions, such as the use of reactors in series, performing polymerisation with a catalyst in the absence of hydrogen (which acts as a chain transfer agent reducing the molecular weight) in the first of these reactors, yielding a high molecular weight fraction, and then passing the polymer through a second reactor in which the polymerisation is continued in the presence

of hydrogen to produce another fraction of lower molecular weight. Examples of this process are the patents by Morita et al., US 4,338,424, Kuroda et al. US 4,414,369, Rafaut US 4,703,094, Kato et al., US 4,420,592. These methods to produce polymers with a multimodal molecular weight distribution are consequently expensive, complicated and require a longer time, and require more complex plant.

[0010] Another way of obtaining these multimodal polymers is through the use of a single reactor, but using mixtures of two or more different catalysts. Each catalyst produces a polymer having a different molecular weight and molecular weight distribution according to the polymerisation reaction rate constants for each catalyst, or as a result of differences in reactive behaviour to different monomers and/or the presence of H₂, e.g. Ewen et al., EP 128045, use mixtures of different metallocenes, with different rates of propagation and reaction with respect to the same monomer. In another patent, EP 128046, Ewen et al. use mixtures of metallocenes with different reactivities to different monomers. With the same object Stricklen et al., US 4,939,217 and US 5,064,797, on the other hand use two or more metallocenes alkylated with MAO, with a different behaviour to H₂, obtaining polymers with different molecular weights. In another patent, WO 9215619, Stricklen et al. effect polymerisation in two stages, the first being a homopolymerisation in the presence of H₂ and the second a copolymerisation in the presence of H₂. Ewen et al., EP 310734, use mixtures of two chiral stereorigid metallocenes for the same purpose. However, it is difficult to control the feed of the two catalysts, and, as the particles are not of uniform size, segregation processes occur during storage and transfer of the polymer resulting in non-homogeneous polymer mixtures.

[0011] This invention claims the manufacture of polymers or copolymers of alpha-olefins with broad bimodal or multimodal molecular weight distributions in a single reactor using catalyst systems which differ from those previously patented in that a single metallocene catalyst is used in combination with mixtures of two or more compounds which act as co-catalysts. These polymers are obtained in good yield and with the good processability characteristics and properties described above.

DETAILED DESCRIPTION OF THE INVENTION

[0012] This invention is characterised by the manufacture of polyolefins having broad bimodal and multimodal molecular weight distributions using a) a single metallocene catalyst and b) at least two co-catalysts as the catalyst system. The system provided has different active centres, with different polymerisation reaction initiation and rate constants as are required for the formation of polymer fractions having different molecular weights. The difference from the other patents described, based on mixtures of catalysts, is the formation of a catalyst system from a single catalyst which is ca-

pable of forming multiple active centres.

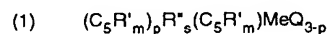
[0013] In particular the polymers according to the invention are ethylene homopolymers, but nevertheless the use of small quantities of higher alpha-olefins having from 3 to 10 carbon atoms and preferably from 4 to 8 carbon atoms can produce ethylene copolymers. Illustrated examples of these higher alpha-olefins are 1-butene, 1-hexene and 1-octene.

[0014] In this invention, ethylene, alone or with smaller quantities of alpha-olefin, is polymerised in the presence of a catalyst system which consists of a) a single metallocene as catalyst and b) at least two compounds as co-catalysts.

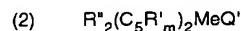
[0015] The invention provides a catalyst system for obtaining homopolymers of alpha-olefins containing from 2 to 20 carbon atoms and copolymers of different alpha-olefins containing from 2 to 20 carbon atoms with wide bimodal or multimodal molecular weight distributions consisting of two subsystems (a) and (b): (a) is a single supported or unsupported metallocene catalyst; and (b) is a mixture of two or more co-catalysts selected from an aluminum compound and a boron compound. The particulars of both subsystems are mentioned below.

[0016] Subsystem (a) is a metallocene catalyst.

[0017] The metallocenes used are organometallic coordination compounds of mono, di or tricyclopentadienyl and their derivatives of transition metal in groups 4b, 5b and 6b of the Periodic Table of Elements, represented by the general formulae:



or



where (C₅R'_m) is cyclopentadienyl or substituted cyclopentadienyl, each R' may be the same or different, and may be hydrogen, monohydrocarbon radicals selected from the group consisting of alkyl, alkenyl, aryl, alkylaryl or arylalkyl containing 1 to 20 carbon atoms, or two adjacent carbon atoms joined to form a C4-C6 ring, or various condensed rings, R* is an alkylene radical containing from 1 to 4 carbon atoms, a dialkyl germanium or silicon radical, or an alkylphosphino or amine radical joining two (C₅R'_m) rings, Q is a hydrocarbon radical selected from the group consisting of aryl alkyl, alkenyl, alkyl aryl, arylalkyl containing from 1 to 20 carbon atoms, or halogen, and each one may be the same or different, Q' is an alkylidene radical containing from 1 to 20 carbon atoms, Me is a transition metal in groups 4b, 5b or 6b of the Periodic Table of elements, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 if s is 1 and m is 5 if s is 0.

[0018] Examples of hydrocarbon radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, and phenyl.

[0019] Examples of alkylene bridges are methylene, ethylene, and propylene.

[0020] Examples of halogen atoms are chlorine, bromine and iodine, the preferred halogen being chlorine.

[0021] Examples of alkylidene radicals are methyldene, ethylidene and propylidene.

[0022] The metallocenes used in accordance with this invention are preferably mono, bis or tris cyclopentadienyl or substituted cyclopentadienyls or Litanium (IV) or zirconium (IV) represented in the general formula.

[0023] Illustrative but not restrictive examples of the metallocenes used in this invention are titanium monocyclopentadienyls such as cyclopentadienyl titanium trichloride, pentamethylcyclopentadienyl titanium trichloride, titanium biscyclopentadienyls such as bis(cyclopentadienyl) titanium dichloride, dimethyl bis(cyclopentadienyl) titanium, diphenyl bis(cyclopentadienyl) titanium, bis(indenyl) titanium dichloride, dimethyl bis(indenyl) titanium, diphenyl bis(cyclopentadienyl) titanium, dialkyl, trialkyl, tetralkyl and pentaalkyl cyclopentadienyl derivatives such as diphenyl or dihalo, bis(1,2-dimethyl cyclopentadienyl) titanium, dimethyl or dihalo bis(1,2-diethyl cyclopentadienyl) titanium and other complex dialkyls or dihalides.

[0024] Illustrative but not restrictive examples of appropriate zirconium metallocenes for use in this invention are zirconium monocyclopentadienyls such as cyclopentadienyl zirconium dichloride, pentamethylcyclopentadienyl zirconium trichloride, zirconium biscyclopentadienyls such as bis(cyclopentadienyl) zirconium dichloride, dimethyl bis(cyclopentadienyl) zirconium, diphenyl bis(cyclopentadienyl) zirconium, substituted cyclopentadienyl alkyls such as dimethyl or dihalo bis(ethylcyclopentadienyl) zirconium, diphenyl or dihalo bis(methylcyclopentadienyl) zirconium, dialkyl, trialkyl, tetralkyl and pentaalkyl cyclopentadienyl (pentamethylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride, dimethyl or dihalo bis(pentamethylcyclopentadienyl) zirconium, and dimethyl bis(1,2-dimethylcyclopentadienyl) zirconium.

[0025] Silicon, phosphorus and carbon bridges between cyclopentadienyl rings such as e.g. dimethyl or dihalo dimethylsilylbis(cyclopentadienyl) zirconium, dimethyl or dihalo methylphosphene bis(cyclopentadienyl) zirconium, dimethyl or dihalo methylene bis(cyclopentadienyl) zirconium, carbenes represented by the formula $CP_2Zr = CH_2P(C_6H_5)_2CH_3$, and derivatives of these compounds such as $CP_2ZrCH_2CH(CH_3)CH_2$.

[0026] Biscyclopentadienyl hafnium dichloride, dimethyl bis(cyclopentadienyl) hafnium, bis(cyclopentadienyl) vanadium dichloride are illustrative of other metallocenes.

[0027] Subsystems (b) is a mixture of two or more co-catalysts selected from the group consisting of (i) aluminoxanes of formula (4) and (ii) specific boron compounds, together with, optionally, a further aluminium compound of formula (3).

[0028] The compounds which can act as co-catalysts in the polymerisation of olefins and which are useful for use in accordance with this invention are well known in the literature, and can be divided into three groups:

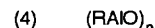
(a) Aluminium compounds of general formula:



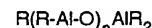
where the R'' groups, which may be the same or different, may be alkyls or aryls containing from 1 to 20 carbon atoms, or halogens, and Al is aluminium.

Illustrative but not restrictive examples of compounds in this group of aluminium compounds are trimethyl aluminium, triethyl aluminium, triisobutyl aluminium, aluminium diethyl chloride, aluminium monoethyl chloride, and triphenyl aluminium.

(b) Aluminium compounds having Al-O bonds (aluminoxanes) of general formula:



or



where R is an alkyl or aryl group containing from 1 to 20 carbon atoms, and n is a number from 1 to 20. These compounds are known in the literature as aluminoxanes and have two different structures, linear and cyclic. In this invention the compound when R = methyl is preferred, i.e. methyl aluminoxane (MAO).

(c) Boron compounds are selected from the group consisting of pentafluorophenyl diphenyl borane, tris(pentafluorophenyl) borane, tris(3,5-di-trifluoromethylphenyl) borane, tributyl ammonium tetrakis(pentafluorophenyl) borate, N,N'-dimethylanilino tetrakis(pentafluorophenyl) borate, tri(methylphenyl)phosphoniumtetrakis(pentafluorophenyl)borate and triphenylcarbene tetrakis(pentafluorophenyl) borate.

[0029] In accordance with this invention these compounds, which act as co-catalysts in the catalytic system together with the metallocene, should take part forming mixtures of at least two compounds for the polymerisation of olefins producing polymers having broad bimodal and multimodal molecular weight distributions.

[0030] Combinations between the three groups of compounds formulated above may be used in this invention, and the following combinations are appropriate:

Aluminium alkyls and aluminoxanes and boron

compounds, and
Aluminoxanes and boron compounds.

[0031] The proportions used in these co-catalyst systems containing more than one co-catalyst vary depending on the metallocene compound used. The molar ratios between the aluminium compounds (aluminium alkyls and/or aluminoxanes) and transition metals of the metallocene vary from 1:1 to 10^8 :1, preferably from 5:1 to 10^5 :1. Molar ratios between aluminium compounds (aluminium alkyls and/or aluminoxanes) and boron compounds vary from 0.01:1 to 10^4 :1, preferably from 0.1:1 to 10^3 :1. The molar ratios used between compounds of boron and the transition metal of the metallocene will be determined by the ratios between the compounds of aluminium and the transition metal and the molar ratios between the aluminium compound and the boron compound.

[0032] The distribution of molecular weights and the incorporation of co-monomer in each fraction of molecular weight is controlled by appropriate selection of the metallocene and combinations to form the mixture of co-catalysts, and the variables H_2 content, pressure and temperature, and the molar ratios between the different components of the catalyst system.

[0033] Broad bimodal or multimodal molecular weight distributions may be obtained by adding the components of the catalyst system, catalyst and co-catalysts, to the reaction medium separately or premixed. Broad bimodal or multimodal distributions can be achieved with addition in any order.

[0034] The solvents used in preparation of the catalytic system are inert hydrocarbons, particularly those inert to the catalyst system, which is sensitive to impurities such as traces of water, oxygen, and air. These solvents are e.g. butane, isobutane, pentane, hexane, heptane, octane, cyclohexane, methyl cyclohexane, toluene, xylene, petroleum fractions from fractions of different boiling point. The co-catalyst described should be used with hydrocarbon solvents such as e.g. toluene or xylene in concentrations from 0.1 M to 3.0 M, although higher or lower concentrations may be used.

[0035] The catalyst systems described in this invention are useful for the polymerisation of α -olefins in solution, slurries or the gas phase over a wide range of temperatures and pressures. For example temperatures may vary from -60°C to 280°C , and preferably from 40°C to 160°C . Pressures vary from 1 to 500 atmospheres or higher. The polymerisation time may vary from 1 minute to 6 hours, but frequently from 10 minutes to 2 hours.

[0036] Polymerisation in solution makes it possible to use the catalyst system as a homogeneous system, but nevertheless the catalyst system may be converted into a heterogeneous system by supporting the metallocene on typical supports, using techniques known in the literature. The supports may be inorganic supports such as silica, silica-alumina, alumina, metal oxides in general,

and MgCl_2 , or may be organic such as polyethylene, polybutadiene, etc. The solid system is more appropriate for slurry or gas phase polymerisation.

[0037] Heterogeneous catalysts are preferable for the production of polymers such as polyethylene, as the active centres are sufficiently fixed and separated on the support, avoiding deactivation reactions between them, and generally -higher molecular weights are obtained. In addition to this the particle shape, size and size distribution of the resulting polymer is better controlled using supported catalysts.

[0038] Polymers obtained according to this invention have average molecular weights which may vary from 500 to 10^7 by weight. It is also possible to use H_2 to control the molecular weight of the polymers formed, but this is not always necessary as it can also be adjusted by varying the molar ratios between the different components of the catalyst system, the metallocene concentrations, the reaction temperature, etc.

[0039] The process of the invention is suitable for obtaining homopolymers of α -olefins containing from 2 to 20 carbon atoms and copolymers of different α -olefins containing from 2 to 20 carbon atoms with wide bimodal or multimodal molecular weight distributions. In a particular embodiment, an ethylene homopolymer is obtained. In other particular embodiment, an ethylene copolymer is obtained by incorporating at random 1-butene, 1-hexene or 1-octene as co-monomer.

[0040] In the examples which follow molecular weights have been determined using a Walters ALC/GPC Model 150C apparatus equipped with a Viscatek 110 viscometer using Polymer Laboratory Columns (2 x mixed bed, 10^7 and another of 10^6). Measurements were performed by dissolving the polymer samples in trichlorobenzene (TCB) at 145°C and filtering them. Irganox 1010 was used as antioxidant. The flow rate was 1 ml/min with concentrations of 1.5 mg/ml.

EXAMPLES

EXAMPLE 1a (not illustrating the claimed invention)

[0041] This example serves to describe the preparation of a polymer having a narrow monomodal distribution when a metallocene and a single co-catalyst of the aluminoxane type is used. A glass reactor of 1 l capacity equipped with a mechanical stirrer, an outer jacket for temperature control, an inlet feed for monomers and gases, an inlet feed with a septum for adding doses of the catalyst system with a syringe, was dried and deoxygenated using a flow of nitrogen. 400 ml of dry n-heptane were added directly with continuous stirring (1200 rpm). The nitrogen atmosphere was removed by charging and discharging the vessel with ethylene until the solution became saturated with ethylene. This was then heated to 90°C and 2.0 mols of methyl aluminoxane (MAO, 1.5 M solution in toluene) were added. After the ethylene pressure increased to 4 bars, 5.84 mg (0.02

mmol) of bis(cyclopentadienyl) zirconium dichloride dissolved in toluene were added using a syringe. After 15 minutes the reactor was depressurised and the reaction mixture cooled. The polymer was discharged and washed with slightly acidified methanol to deactivate catalyst residues and dried to constant weight in a vacuum stove. 27.89 g of white polyethylene powder were obtained with an average molecular weight of 69000 and a polydispersity index of $M_w/M_n = 3.5$. The molecular weight distribution was narrow and monomodal.

EXAMPLE 1b (not illustrating the claimed invention)

[0042] This example serves to describe the preparation of a polymer having a narrow monomodal distribution when an alkylated metallocene and a single co-catalyst of the boron compound type is used. From a flask of 500 ml capacity equipped with septum inlets and a magnetic stirrer oxygen was removed by displacement with flows of nitrogen and 200 ml of dry N-heptane were injected. This was then placed in a thermostatic bath and the nitrogen atmosphere was replaced by ethylene by successive charging and discharging with ethylene. 51.2 mg (0.1 mmoles) of tris(pentafluorophenyl) borane dissolved in toluene (0.1 M) were introduced into the flask through the septum using a syringe with a hypodermic needle. When the solution was saturated with ethylene and the temperature was 40°C, 25.0 mg (0.1 mmoles) of dimethyl bis(cyclopentadienyl) zirconium dissolved in toluene (0.1 M) were injected directly into the flask. After 15 minutes reaction 6.92 g of polyethylene having a molecular weight of $M_w = 189,000$ and a polydispersity index of $M_w/M_n = 2.4$ were obtained. The molecular weight distribution was narrow and monomodal. Both the CP_2ZrMe_2 and the $B(C_6F_5)_3$ were prepared in accordance with the methods described in the literature.

[0043] The ten examples which follow describe the production of a bimodal homopolymer or copolymer according to the method described in this invention.

EXAMPLE 2

[0044] This example describes the preparation of a bimodal polyethylene. 200 ml of dry n-heptane were injected under a nitrogen atmosphere into a dry 500 ml capacity flask from which oxygen had been removed using a flow of nitrogen, equipped with inlets provided with a septum and a magnetic stirrer. This was then placed in a thermostatic bath and the nitrogen atmosphere was replaced with ethylene by successive charging and discharging with ethylene. 10.0 mmoles of methylaluminoxane and subsequently 51.2 mg (0.1 mmoles) of tris(pentafluorophenyl) borane dissolved in toluene (0.1 M) were introduced using a syringe with a hypodermic needle. When the solution was saturated with ethylene and the temperature was 40°C, 29.2 mg (0.1 mmoles) of bis(cyclopentadienyl)zirconium dichloride dissolved in toluene (0.1 M) were injected directly into the flask. After

15 minutes reaction a polymer was obtained which was shown to be clearly bimodal when analysed by GPC. The molecular weight $M_w = 108,900$ and the polydispersity $M_w/M_n = 11.54$.

EXAMPLE 3

[0045] This example describes the preparation of a bimodal polyethylene. The method for preparing the polyethylene is similar to the procedure described in Example 2, but the boron compound was injected first, followed by the metallocene and finally the aluminoxane. The resulting polyethylene had a $M_w = 86,600$ and a polydispersity of $M_w/M_n = 12.51$, the molecular weight distribution of the polymer being clearly bimodal, as shown by its chromatogram.

EXAMPLE 4

[0046] This example describes the preparation of a bimodal polyethylene. This was prepared using the procedure described in Example 2, but first injecting a prepared mixture of methylaluminoxane and bis(cyclopentadienyl) zirconium dichloride in a molar ratio 10:1 which had been aged for 24 hours and in quantities such that the concentrations in the flask were 6.0 mmoles of MAO and 0.06 mmoles of CP_2ZrCl_2 . 0.1 mmoles of $B(C_6F_5)_3$ were then added. The polyethylene had a molecular weight of $M_w = 115,500$ and a polydispersity of $M_w/M_n = 10.35$. The resulting chromatogram was clearly bimodal.

EXAMPLE 5

[0047] This example describes the preparation of a bimodal polyethylene. The preparation was in accordance with the procedure described in Example 1a, but 10.0 mmoles of methylaluminoxane and 0.05 mmoles of $B(C_6F_5)_3$ were injected prior to injecting 14.62 mg (0.06 mmoles) of bis(cyclopentadienyl) zirconium dichloride. The chromatogram of the resulting polymer showed a bimodal molecular weight distribution as shown in the chromatogram in Figure 1.

EXAMPLE 6

[0048] This example describes the preparation of a bimodal ethylene-hexene copolymer. The copolymer in this example was prepared in accordance with the procedure described in Example 1a, adding 1.97 ml (15.87 mmoles) of 1-hexene when the reactor was saturated with ethylene and at 40°C. Once this had been added the temperature was raised to 90°C. 2.0 mmoles of MAO, 0.02 mmoles of $B(C_6F_5)_3$ and 0.02 mmoles of zirconocene were then added. After 15 minutes reaction 27.07 g of a polyethylene having a molecular weight of $M_w = 62,400$ and a polydispersity of $M_w/M_n = 8.2$, with

a clearly bimodal chromatogram, were obtained.

EXAMPLE 7

[0049] This example describes the preparation of a bimodal polyethylene. The polyethylene in this example was prepared in accordance with the procedure described in Example 1a, but adding 2.0 mmoles of MAO and 0.02 mmoles of $B(C_6F_5)_3$. The reaction was completed in the presence of 0.2 bar of hydrogen. After 15 minutes reaction 28.31 g of a polyethylene whose molecular weight distribution from the chromatogram was clearly bimodal, as shown by the chromatogram in Figure 2, was obtained.

EXAMPLE 8

[0050] This example describes the preparation of a bimodal polyethylene. It was prepared in accordance with the procedure described in Example 2, but using 50.0 mmoles of methylaluminoxane, 0.1 mmoles of $B(C_6F_5)_3$ and 36.23 mg (0.1 mmoles) of (pentamethylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride. The resulting polymer yielded a bimodal chromatogram, had a molecular weight of $M_w = 105,900$ and a polydispersity of $M_w/M_n = 8.57$. The zirconocene was synthesised in accordance with the methods described in the literature.

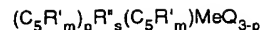
EXAMPLE 9

[0051] This example describes the preparation of a bimodal polyethylene. It was prepared in accordance with the procedure described in Example 2, but using 15.0 mmoles of methyl aluminoxane, 7.5 mmoles of triisobutylaluminium 0.1 inmoles of $B(C_6F_5)_3$ and 29.02 mg (0.1 mmoles) of biscyclopentadienyl zirconium dichloride. The polymer had a molecular weight of $M_w = 97,500$ and a polydispersity of $M_w/M_n = 6.89$. The molecular weight distribution as shown by the GPC chromatogram was clearly bimodal.

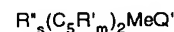
Claims

1. A catalyst system for obtaining homopolymers of alpha-olefins containing from 2 to 20 carbon atoms and copolymers of different alpha-olefins containing from 2 to 20 carbon atoms with wide bimodal or multimodal molecular weight distributions, consisting of two subsystem (a) and (b):

(a) a single supported or unsupported metallocene catalyst, being mono, di or tricyclopentadienyl and their derivatives of transition metals in groups 4b, 5b, 6b of the Periodic Table of elements, represented by the general formulae:



or



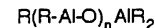
where $(C_5R'_m)$ is cyclopentadienyl or substituted cyclopentadienyl, each R' may be the same or different, and may be hydrogen, monohydrocarbon radicals selected from the group consisting of alkyl, alkenyl, aryl, alkylaryl or arylalkyl containing from 1 to 20 carbon atoms, or two adjacent carbon atoms joined to form a C4-C6 ring, or various condensed rings, R'' is an alkylene radical containing from 1 to 4 carbon atoms, a dialkyl germanium or silicon radical, or an alkylphosphine or amino radical joining two $(C_5R'_m)$ rings, Q is a hydrocarbon radical selected from the group consisting of: aryl, alkyl, alkenyl, alkylaryl, arylalkyl containing from 1 to 20 carbon atoms, or halogen, and each one may be the same or different, Q' is an alkylidene radical containing from 1 to 20 carbon atoms, Me is a transition metal in groups 4b, 5b or 6b of the Periodic Table of elements, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 if s is 1 and m is 5 if s is 0;

(b) a mixture of two or more co-catalysts selected from the following groups i) and ii):

i) Aluminum compounds having Al-O bonds (Aluminoxanes) corresponding to the general formulae:



or



where R is an alkyl or aryl group containing from 1 to 20 carbon atoms, and n is a number from 1 to 20;

ii) Boron compounds selected from the group consisting of pentafluorophenyl diphenyl borane, tris(pentafluorophenyl) borane, tris(3,5-di-trifluoromethylphenyl) borane, tributyl ammonium tetrakis(pentafluorophenyl) borate, N,N'-dimethylanilino tetrakis(pentafluorophenyl) borate, tri(methylphenyl) phosphoniumtetrakis(pentafluorophenyl) borate and triphenylcarbene tetrakis(pentafluorophenyl) borate.

2. Catalytic system according to claim 1 further comprising an aluminium compound of general formula



where the R'' groups, which may be the same or different, may be alkyls or aryls containing from 1 to 20 carbon atoms, or halogens, and Al is aluminium.

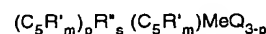
3. Catalyst system according to claim 2 wherein the metallocene is supported or unsupported by (cyclopentadienyl) zirconium dichloride, the aluminium compound is selected from trimethylaluminum, triethylaluminum or triisobutylaluminum, the boron compound is tris(pentafluorophenyl) borane and the aluminosilane is methylaluminosilane.
4. Catalyst system according to claims 1-3, wherein the molar ratios between the aluminium compounds (aluminium alkyls and/or aluminosilanes) and transition metals of the metallocene varies from 1.0:1.0 to 10⁸:1.0 and the molar ratios between the aluminium compounds (aluminium alkyls and/or aluminosilanes) and boron compounds varies from 0.01:1 to 10⁴:1.
5. Catalyst system according to claim 4, wherein the molar ratios between the aluminium compounds (aluminium alkyls and/or aluminosilanes) and transition metals of the metallocene varies from 5.0:1.0 to 10⁵:1.0 and the molar ratios between the aluminium compounds (aluminium alkyls and/or aluminosilanes) and boron compounds varies from 0.1:1 to 10³:1.0.
6. Process for the preparation of homopolymers of alpha-olefins containing from 2 to 20 carbon atoms and copolymers of different alpha-olefins containing from 2 to 20 carbon atoms with wide bimodal or multimodal molecular weight distributions, in a single reactor characterized by use of the catalytic system of claims 1-5.
7. Process for the preparation of homopolymers according to claim 6, wherein the olefin is ethylene.
8. Process for the preparation of ethylene copolymers according to claim 6, wherein the co-monomer is selected from the group consisting of: 1-butene, 1-hexene or 1-octene and is incorporated at random.
9. Process for the preparation of homopolymers and copolymers according to claims 6-8, characterized by the use of hydrocarbon solvents under inert conditions for the catalytic system and reaction temper-

atures between -60°C and 280°C, preferably between 40°C and 160°C, reactor pressures between 1 and 500 atmospheres.

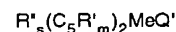
Patentansprüche

1. Ein Katalysatorsystem zur Herstellung von Alpha-olefinhomopolymeren, die 2 bis 20 Kohlenstoffatome enthalten, und Copolymere verschiedener Alpha-olefine, die 2 bis 20 Kohlenstoffatome enthalten, mit einer breiten bimodalen oder multimodalen Verteilung der Molekulargewichte, welches aus zwei Untersystemen (a) und (b) besteht:

(a) einem Katalysator aus individuellem, getragenen oder nicht getragenen Metallocen, das Mono-, Di- oder Tricyclopentadienyl und dessen Derivate der Übergangsmetalle der Gruppen 4b, 5b oder 6b des Periodensystems der Elemente ist, dargestellt durch die allgemeinen Formeln



oder



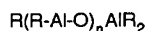
in welchen (C₅R'_m) für Cyclopentadienyl oder substituiertes Cyclopentadienyl steht, jedes R' gleich oder verschieden sein kann und für Wasserstoff, für Kohlenwasserstoffradikale ausgewählt aus der aus Alkyl, Alkenyl, Aryl, Alkylaryl oder Arylalkyl bestehenden Gruppe, die 1 bis 20 Kohlenstoffatome enthält, oder für zwei benachbarte, zur Bildung eines C₄-C₆-Ringes verbundene Kohlenstoffatome oder für verschiedene kondensierte Ringe steht, R'' für ein Alkylradikal, das 1 bis 4 Kohlenstoffatome enthält, für ein Dialkylgermanium oder -siliziumradikal, oder für ein Alkylphosphinradikal oder Aminradikal, das zwei (C₅R'_m)-Ringe verbindet, steht, Q für ein Kohlenwasserstoffradikal ausgewählt aus der Gruppe bestehend aus: Aryl, Alkyl, Alkenyl, Alkylaryl, Arylalkyl, die 1 bis 20 Kohlenstoffatome enthält, oder für Halogen steht, wobei jedes gleich oder von den anderen verschieden sein kann, Q' für ein Alkylidenradikal, das 1 bis 20 Kohlenstoffatome enthält, steht, Me für ein Übergangsmetall aus den Gruppen 4b, 5b oder 6b des Periodensystems der Elemente steht, s für 0 oder 1 steht, p für 0, 1 oder 2 steht; und wenn p 0 ist, ist s 1; und m ist 4 wenn s 1 ist und m ist 5 wenn s 0 ist; (b) einer Mischung aus zwei oder mehreren

Cokatalysatoren ausgewählt aus den folgenden Gruppen i) und ii):

- i) Aluminiumverbindungen, die Al-O-Bindungen (Aluminoxane) enthalten, die den allgemeinen Formeln:



oder



in welchen R für eine Alkyl- oder Arylgruppe steht, die 1 bis 20 Kohlenstoffatome enthält und n für eine Zahl zwischen 1 und 20 steht, entsprechen;

- ii) Borverbindungen ausgewählt aus der Gruppe bestehend aus Pentafluorphenyldiphenylboran, Tris(pentafluorphenyl)boran, Tris(3,5-di-trifluormethylphenyl)boran, Tributylammonium-Tetrakis(pentafluorphenyl)borat, N,N'-Dimethylanilin-Tetrakis(pentafluorphenyl)borat, Tri(methylphenyl)phosponium-Tetrakis(pentafluorphenyl)borat und Triphenylkarben-Tetrakis(pentafluorphenyl)borat.

2. Katalysatorsystem gemäss Anspruch 1, welches ausserdem eine Aluminiumverbindung der allgemeinen Formel enthält:



in welcher die R''-Gruppen, die gleich oder verschieden sein können, für Alkyle oder Aryle, die 1 bis 20 Kohlenstoffatome enthalten, oder für Halogene stehen können, und Al für Aluminium steht.

3. Katalysatorsystem gemäss Anspruch 2, in welchem das Metallocen ein getragenes oder nicht getragenes Bis(cyclopentadienyl)zirkoniumdichlorid ist, die Aluminiumverbindung unter Trimethylaluminium, Triethylaluminium oder Triisobutylaluminium ausgewählt ist, und die Borverbindung ein Tris(pentafluorphenyl)boran ist und das Aluminoxan ein Methylaluminoxan ist.

4. Katalysatorsystem gemäss den Ansprüchen 1-3, in welchem die Molverhältnisse zwischen den Aluminiumverbindungen (Alkylaluminium und/oder Aluminoxane) und den Übergangsmetallen des Metallocens zwischen 1,0:1,0 und 10⁸:1,0 liegen und die Molverhältnisse zwischen den Aluminiumverbindungen (Alkylaluminium und/oder Aluminoxane)

und den Borverbindungen zwischen 0,01:1 und 10⁴:1 liegen.

5. Katalysatorsystem gemäss Anspruch 4, in welchem die Molverhältnisse zwischen den Aluminiumverbindungen (Alkylaluminium und/oder Aluminoxane) und den Übergangsmetallen des Metallocens zwischen 5,0:1,0 und 10⁵:1,0 liegen und die Molverhältnisse zwischen den Aluminiumverbindungen (Alkylaluminium und/oder Aluminoxane) und den Borverbindungen zwischen 0,1:1 und 10³:1,0 liegen.

6. Verfahren zur Herstellung von Alphaolefinhomopolymeren, die 2 bis 20 Kohlenstoffatome enthalten, und Copolymere verschiedener Alphaolefine, die 2 bis 20 Kohlenstoffatome enthalten, mit einer breiten bimodalen oder multimodalen Verteilung der Molekulargewichte, in einem einzigen Reaktor, gekennzeichnet durch die Verwendung des Katalysatorsystems gemäss den Ansprüchen 1-5.

7. Verfahren zur Herstellung von Homopolymeren gemäss Anspruch 6, bei welchem das Olefin Ethylen ist.

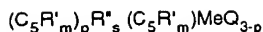
8. Verfahren zur Herstellung von Ethylencopolymeren gemäss Anspruch 6, bei welchem das Comonomer aus der Gruppe bestehend aus: 1-Buten, 1-Hexen oder 1-Okten ausgewählt wird und aleatorisch eingefügt wird.

9. Verfahren zur Herstellung von Homopolymeren und Copolymeren gemäss Anspruch 6, gekennzeichnet durch die Verwendung von kohlenwasserstoffhaltigen Lösemitteln unter inerten Bedingungen für das Katalysatorsystem, bei Reaktionstemperaturen zwischen -60°C und 280°C, vorzugsweise zwischen 40°C und 160°C, und bei Reaktordrücken zwischen 1 und 500 Atmosphären.

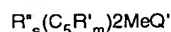
Revendications

1. Un système catalyseur pour obtenir des homopolymères d'alpha-oléfines qui contiennent de 2 à 20 atomes de carbone et des copolymères de différentes alpha-oléfines qui contiennent de 2 à 20 atomes de carbone, avec de larges distributions bimodales ou multimodales de poids moléculaires, qui est composé de deux sous-systèmes (a) et (b) :

(a) un catalyseur de metallocène individuel supporté ou non supporté, qui est mono, di ou tricyclopentadiényle et ses dérivés de métaux de transition des groupes 4b, 5b ou 6b de la Table Périodique des éléments, représenté par les formules générales



ou

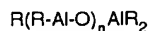


dans lesquelles $(C_5R'_m)$ est cyclopentadiényle ou cyclopentadiényle substitué, chaque R' peut être pareil ou différent et peut être de l'hydrogène, des radicaux hydrocarbonés sélectionnés parmi le groupe composé par alcoyle, alkényle, aryle, alcoylaryle ou arylalcoyle qui contient de 1 à 20 atomes de carbone, ou deux atomes de carbone adjacents unis pour former un anneau C_4-C_6 , ou plusieurs anneaux condensés, R'' est un radical alkényle qui contient de 1 à 4 atomes de carbone, un radical de dialcoyle germanium ou silice, ou un radical alcoylphosphine ou amine qui unit deux anneaux $(C_5R'_m)$, Q est un radical hydrocarboné sélectionné parmi le groupe composé par : aryle, alcoyle, alkényle, alcoylaryle, arylalcoyle qui contient de 1 à 20 atomes de carbone, ou halogène, et chacun peut être pareil ou différent des autres, Q' est un radical alcoylidène qui contient de 1 à 20 atomes de carbone, Me est un métal de transition des groupes 4b, 5b ou 6b de la Table Périodique des éléments, s est 0 ou 1, p est 0, 1 ou 2 ; lorsque p est 0, s est 1 ; m est 4 si s est 1 et m est 5 si s est 0 ; (b) un mélange de deux ou plusieurs co-catalyseurs sélectionnés parmi les groupes i) et ii) suivants :

i) composés d'aluminium qui ont des liaisons Al-O (Aluminoxanes) qui correspondent aux formules générales :



ou



dans lesquelles R est un groupe alcoyle ou aryle qui contient de 1 à 20 atomes de carbone, et n est un nombre de 1 à 20 ;
ii) composés de bore sélectionnés parmi le groupe composé par pentafluorophényl diphenyl borane, tris(pentafluorophényl)borane, tris(3,5-di-trifluorométhylphényl)borane, tétraquis(pentafluorophényl) borate de tributyl ammonium, tétraquis(pentafluorophényl)borate de N,N'-diméthylaniline,

tétraquis(pentafluorophényl)borate de tri(méthylphényl)phosphonium et tétraquis(pentafluorophényl)borate de triphénylcarbène.

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2. Système catalytique selon la revendication 1, qui comprend en outre un composé d'aluminium de formule générale :



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dans laquelle les groupes R'' , qui peuvent être pareils ou différents, peuvent être des alcoyles ou des aryles qui contiennent de 1 à 20 atomes de carbone, ou des halogènes, et Al est aluminium.

3. Système catalyseur selon la revendication 2, dans lequel le métallocène est du dichlorure de bis(cyclopentadiényl)zirconium supporté ou non supporté, le composé d'aluminium se sélectionne entre le triméthylaluminium, le triéthylaluminium ou le triisobutylaluminium, le composé de bore est du tris(pentafluorophényl)borane et l'aluminoxane est du méthylaluminoxane.

4. Système catalyseur selon les revendications 1-3, dans lequel les relations molaires entre les composés d'aluminium (alcoyl aluminiums et/ou aluminoxanes) et les métaux de transition du métallocène varient entre 1,0:1,0 et 10^6 :1,0 et les relations molaires entre les composés d'aluminium (alcoyl aluminiums et/ou aluminoxanes) et les composés de bore varient entre 0,01:1 et 10^4 :1.

5. Système catalyseur selon la revendication 4, dans lequel les relations molaires entre les composés d'aluminium (alcoyl aluminiums et/ou aluminoxanes) et les métaux de transition du métallocène varient entre 5,0:1,0 et 10^5 :1,0 et les relations molaires entre les composés d'aluminium (alcoyl aluminiums et/ou aluminoxanes) et les composés de bore varient entre 0,1:1 et 10^3 :1,0.

6. Procédé pour la préparation d'homopolymères d'alpha-oléfines qui contiennent de 2 à 20 atomes de carbone et de copolymères de différentes alpha-oléfines qui contiennent de 2 à 20 atomes de carbone avec une large distribution bimodale ou multimodale de poids moléculaires dans un seul réacteur, caractérisé par l'utilisation du système catalytique des revendications 1-5.

7. Procédé pour la préparation d'homopolymères selon la revendication 6, dans lequel l'oléfine est de l'éthylène.

8. Procédé pour la préparation de copolymères

d'éthylène selon la revendication 6, dans lequel le co-monomère se sélectionne parmi le groupe composé par : 1-butène, 1-hexène o 1-octène et où il s'incorpore de façon aléatoire.

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9. Procédé pour la préparation d'homopolymères et de copolymères selon les revendications 6-8, caractérisé par l'utilisation de solvants hydrocarbonés sous des conditions inertes pour le système catalyseur, températures de réaction comprises entre 10
-60°C et 280°C, de préférence entre 40°C et 160°C, et pressions du réacteur comprises entre 1 et 500 atmosphères.

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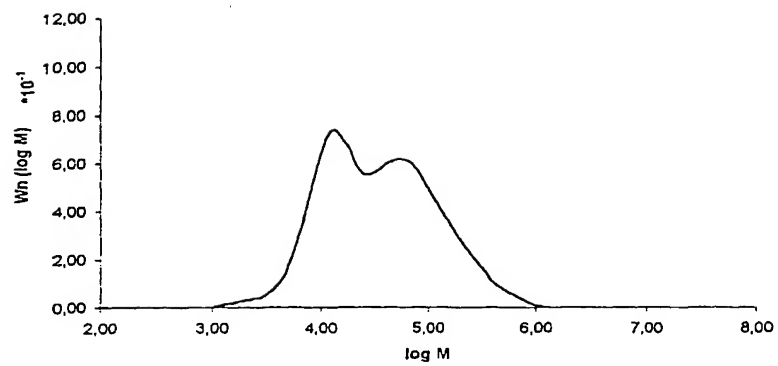


Fig.1

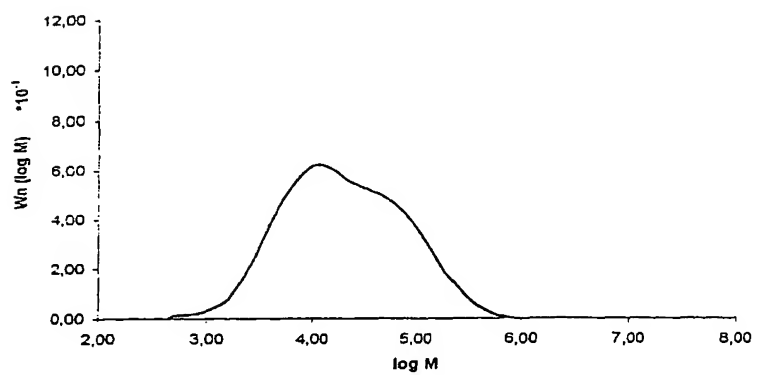


Fig.2